

Surface Science Letters

Molecularly intact and dissociative adsorption of water on clean Cu(110): A comparison with the water/Ru(001) system

K. Andersson^{a,b}, A. Gómez^b, C. Glover^c, D. Nordlund^{a,b},
H. Öström^b, T. Schiros^{a,b}, O. Takahashi^{b,d}, H. Ogasawara^{a,b,*},
L.G.M. Pettersson^b, A. Nilsson^{a,b}

^a *Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA*

^b *FYSIKUM, Stockholm University, Albanova University Center, S-10691 Stockholm, Sweden*

^c *Research School of Physical Sciences and Engineering, Australian National University, Canberra 0200, Australia*

^d *Department of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima 739-8526, Japan*

Received 28 October 2004; accepted for publication 15 April 2005

Available online 13 May 2005

Abstract

An X-ray photoelectron spectroscopy (XPS) study was undertaken of the water/Cu(110)-system finding non-dissociative adsorption on clean Cu(110) at temperatures below 150 K. Thermally induced dissociation of D₂O is observed to occur above 150 K, similar to the H₂O/Ru(001) system, with an experimentally derived activation barrier of 0.53–0.56 eV which is very close in magnitude to the derived activation barrier for desorption of 0.50–0.53 eV. X-ray and electron induced damage to the water overlayer was quantified and used to rationalize the results of a recent XPS study of the water/Cu(110)-system where partial dissociation was observed already at 90 K.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Molecule–solid reactions; Synchrotron radiation photoelectron spectroscopy; Radiation damage; Surface chemical reaction; Water; Copper; Ruthenium; Low index single crystal surfaces

1. Introduction

Water adsorption experiments on certain metal substrates, e. g. Cu(110) and Ru(001), have historically, and also recently, been the subject of controversy over the adsorption mechanism being molecular or dissociative [1–7]. Considering the importance of water–metal interactions to, for

* Corresponding author. Address: Stanford Synchrotron Radiation Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA. Tel.: +1 6509264010; fax: +1 6509264100.

E-mail address: hirohito@slac.stanford.edu (H. Ogasawara).

example, electrolysis, fuel cell technology, and corrosion etc., it is essential to settle this controversy by additional experimental studies. The Cu(110) and Ru(001) surfaces are particularly interesting cases since both have been classified by thermodynamic analysis to be borderline cases between molecular and dissociative adsorption of water [1].

Partial dissociation of water under ultra-high vacuum (UHV) conditions and low temperatures (<150 K, i.e. 5 K above water multilayer desorption onset at approximately 145 K) on Cu(110) and Ru(001) has previously been observed using electron based techniques such as low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [2–5]. However, when necessary precautions were taken in a recent XPS study against X-ray and electron induced dissociation for the very sensitive water overlayer on Ru(001) it was found that water adsorbs intact on Ru(001) below 150 K [8]. Analysis of the XP spectra showed that all water molecules in the molecularly intact wetting layer bind directly to the surface suggesting an adsorption model where water bonds to the Ru(001) surface through alternating metal–oxygen (M–O) and metal–hydrogen (M–HO) bonds [8], similar to water adsorption on Pt(111) [9]. The intact water adsorption on Ru(001) is in agreement with conclusions from vibrational spectroscopy studies [7,11–14] where spectral features were assigned to the intact adsorption model consisting of alternating M–O and M–HO bonds [7]. However, thermally induced dissociation of H₂O (not D₂O) on Ru(001) has been observed at temperatures above 150 K [8,14], explaining the anomalous isotope effects in the thermal desorption spectra [10]. The results in [8,14] put the activation barrier towards thermally induced dissociation for the initially molecularly intact monolayer H₂O/Ru(001) system in the 0.45–0.5 eV range in rather good agreement with recent theoretical work on the dissociation barrier of water on Ru(001) calculated to be 0.5–0.65 eV [15,16].

Herein, we report an investigation of the water/Cu(110) system by XPS aimed at determining whether water adsorbs dissociatively or not. Binding energies and related shifts of O 1s core levels as

probed by XPS provide direct evidence for the presence or absence of dissociated species. We find that water adsorbs intact at temperatures below 150 K when sufficient precautions are taken to avoid X-ray and electron induced beam-damage. However, we do find that partial dissociation is induced thermally at temperatures above 150 K, with an experimentally derived activation barrier for D₂O of 0.53–0.56 eV even in the absence of atomic oxygen (in our study below 0.1%) which is known to substantially lower the activation barrier towards water dissociation on Cu(110) [2,17–20]. That water remains intact on Cu(110) below 150 K directly contradicts results of Ammon et al. [3], also utilizing XPS, who claim that partial dissociation occurred already at 90 K. Dissociation of water at 90 K would correspond to a very low activation barrier with an *upper limit* of 0.3 eV. Our results showing water dissociation on clean Cu(110) only above 150 K are similar to the findings for the H₂O/Ru(001) system [8,14].

2. Experimental section

The synchrotron based XPS experiments were performed at the undulator beamline 11.0.2 at the Advanced Light Source (Berkeley, USA) and undulator beamline I511 at MAX-lab (Lund, Sweden) [21]. The vacuum chamber with operating pressure lower than 7×10^{-11} Torr was equipped with low energy electron diffraction (LEED) optics, mass spectrometer, ion-gun, partial electron yield detector and Scienta electron analyzer (SES-100 at the Advanced Light Source and SES-200 at MAX-lab, respectively). The electron spectrometer used to detect photoelectrons was situated directly along the E-vector of the linearly (horizontally) polarized synchrotron radiation (SR) from the undulator in order to be in direct line of sight of the central cone of emitted photoelectrons. O 1s XP spectra were recorded with total energy resolution better than 100 meV at a photon energy of 700 eV. The Cu(110) crystal was cleaned by cycles of Ne⁺- or Ar⁺-sputtering and annealing to 850 K until a sharp 1×1 LEED pattern was observed. Surface contami-

nants such as C and O were below detection limits of XPS ($<0.1\%$) in our experiments. We estimate an upper limit of 1% of surface H-contamination from residual hydrogen in our vacuum chamber based on the low operating pressure during the 10–15 min duration of the experiments.

The temperature of the sample was monitored by a K-type (chromel–alumel) thermocouple located inside a special pocket of the sample for good thermal contact. Heating was performed through a W-filament at the backside of the sample. Electron bombardment heating was employed during sputter–anneal cycles whereas radiative heating with unbiased sample was chosen when water was present on the Cu(110) surface to avoid electron-induced dissociation.

D₂O of 99% isotopic purity was initially cleaned by multiple freeze–pump–thaw cycles, then by distillation and its purity was checked by mass spectrometry prior to experiments. The D₂O-dosing rate onto the sample was regulated by the backing pressure before a pinhole at the backside of an array of multichannel plates [22]. The D₂O coverage was calibrated, using the O 1s XPS intensity, against the saturation coverage of CO at 90 K which is 0.8 monolayer (ML) with respect to the number density of Cu-atoms in the top surface plane [23].

The estimated dissociation probability of a water molecule per electron in the electron distribution generated by 785 eV photons from data of the molecularly intact monolayer on Ru(001) [8] is 9×10^{-2} for H₂O and 4×10^{-2} for D₂O, respectively. The approximately 2-fold lower probability of X-ray and electron induced dissociation for D₂O compared to H₂O motivated our choice of D₂O as adsorbate in this study. However, the choice of D₂O was not sufficient to avoid beam-damage and further measures were required to minimize the critical parameter photon/electron dose per water molecule while still being able to record spectra with reasonable statistics. The photon flux was reduced to generate a sample current of about 2 nA from electrons escaping the substrate surface after having been created in the photo-ionization processes and subsequent inelastic electron scattering events. The use of a 3–5°

grazing incidence of the focused X-ray beam increased the illuminated area producing a $0.1(v) \times 2(h) \text{ mm}^2$ spot on the sample which could still be fully imaged by the electron spectrometer. Finally, and most importantly, the sample was scanned in front of the electron spectrometer while recording XP spectra. Scanning was done at typical speeds of $5\text{--}40 \mu\text{m s}^{-1}$ by the use of computer controlled stepper motors. While scanning it is essential to maintain a constant transmission of electrons through the spectrometer for the acquired kinetic energy range irrespective of sample coordinate. The beam and scanning conditions ensured that the same spot was irradiated for a maximum of 30 seconds and each O 1s XP spectrum was therefore taken at a fresh spot on the sample with a low total photon dose generating an estimated $0.1 \text{ e}^-/\text{water molecule}$ ($20 \mu\text{C cm}^{-2}$); evidently low enough not to lead to any observable beam induced damage of D₂O on Cu(110).

3. Results and discussion

Non-dissociative adsorption of water on the Cu(110) substrate at low temperatures below the multilayer desorption threshold was confirmed by performing time resolved O 1s XPS studies under a constant D₂O flux of about $5 \times 10^{12} \text{ molecules cm}^{-2} \text{ s}^{-1}$ impinging on the Cu(110) surface, i.e. water coverage-dependent O 1s XPS. When the Cu(110) surface was held at 135 K, i.e. approximately 10 K below the multilayer desorption threshold, the O 1s XP spectra consisted simply of a broad peak (FWHM = 1.4 eV) with a maximum at 533.4 eV up to 1 ML coverage as in Fig. 1(a). We observe no evidence for a peak at $\sim 531.0 \text{ eV}$ (hydroxyl) which would indicate dissociation. Above 1 ML we see a high binding energy shoulder beginning to increase in intensity in Fig. 1(a) which is assigned to the onset of water multilayer growth ($\sim 534.3 \text{ eV}$ for the 2nd ML) and this observation is consistent with the saturation coverage of water on Cu(110) being 1 ML. A coverage-dependent O 1s XPS study of D₂O on Cu(110) was also performed at 90 K to ensure the same thermal conditions as in the study in Ref. [3].

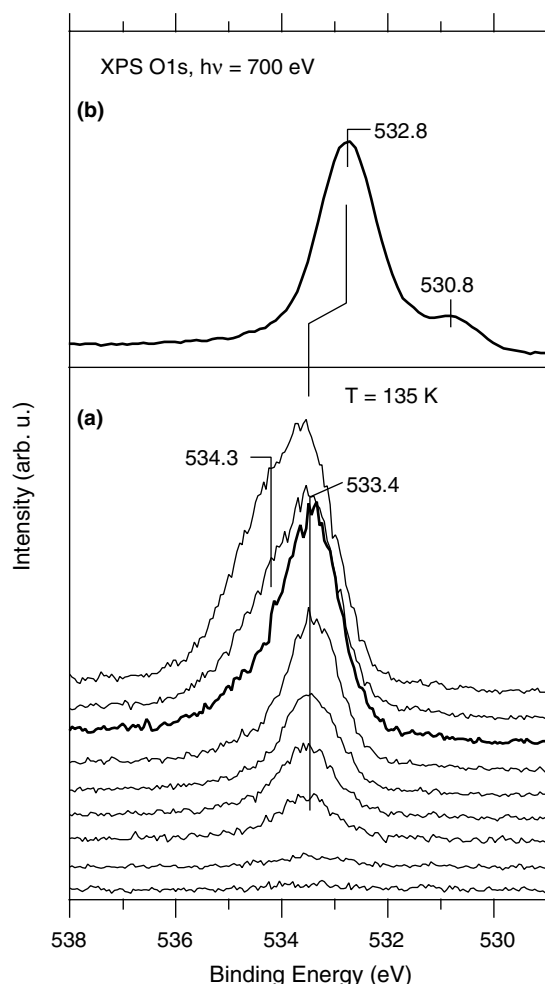


Fig. 1. (a) Time resolved O 1s XPS study performed under a constant D₂O flux of about 5×10^{12} molecules $\text{cm}^{-2} \text{s}^{-1}$ impinging on the Cu(110) surface held at 135 K, i. e. approximately 10 K below the multilayer desorption threshold. Each spectrum was taken at a fresh spot on the sample, due to the sample scanning procedure, with a low total 700 eV photon dose generating $0.1 \text{ e}^-/\text{water molecule}$ and recorded at 36 s intervals. No evidence for hydroxyls ($\sim 531.0 \text{ eV}$) can be observed. Thick solid line corresponds to 1 ML D₂O coverage above which multilayer growth at a binding energy of 534.3 eV starts. (b) 1 ML D₂O exposed to 700 eV photons generating a total dose of $7\text{--}8 \text{ e}^-/\text{water molecule}$. Clear evidence for beam induced dissociation is observed at 530.8 eV (hydroxyls). A shift in binding energy of molecular D₂O from 533.4 eV to 532.8 eV is observed and indicated in the figure with a thin solid line.

However, we observed no dissociation at 90 K either.

When applying electron based techniques such as LEED and XPS, low energy electrons are the main agents for beam-damage to the water overlayer. Electron induced damage to the water overlayer in the water/Cu(110) system has been discussed in LEED experiments by Bange et al. [19] who found that electron exposures of about $6 \text{ e}^-/\text{water molecule}$ (1.2 mC cm^{-2}) caused the water induced $c(2 \times 2)$ LEED pattern to disappear. We performed experiments to quantify and establish the nature of beam induced damage to our sample using XPS. A significant fraction of dissociated water molecules (hydroxyls at 530.8 eV) appeared when 700 eV photons generating a total dose of $7\text{--}8 \text{ e}^-/\text{water molecule}$ ($1.4\text{--}1.6 \text{ mC cm}^{-2}$) was applied to 1 ML water on Cu(110), see Fig. 1(b). We also notice the O 1s binding energy of molecular D₂O in Fig. 1(b) undergo a downward shift from 533.4 eV to 532.8 eV in response to the new environment at the surface. XP spectra in Ref. [3] were recorded from single spots on the sample without a sample scanning procedure and therefore most likely suffered from effects of beam damage to the water overlayer in spite of attempts to avoid it. It is important to note that although care must be taken to ensure the integrity of the molecularly intact water overlayer on Cu(110), we find that this system actually has a factor of at least 3 times *lower* probability ($\sim 1.6 \times 10^{-2}$) for electron induced dissociation by electrons generated from X-rays than the water/Ru(001) system [8].

We have so far established that water adsorption on Cu(110) occurs non-dissociatively below 135 K when sufficient precautions to avoid beam-damage are taken. Bearing in mind that water dissociation is an activated process and that, similar to Ru(001), the Cu(110) surface has been classified to be borderline with regards to water dissociation, water dissociation may be possible on Cu(110) at temperatures above 135 K.

We explored this possibility by performing a temperature dependent XPS study in the 140–195 K range with approximately 1.6 ML D₂O initially present at the Cu(110) surface (Fig. 2). We find that hydroxyl groups ($\sim 531.0 \text{ eV}$) start appearing in the 160–165 K range and increases to a limited but significant hydroxyl surface cover-

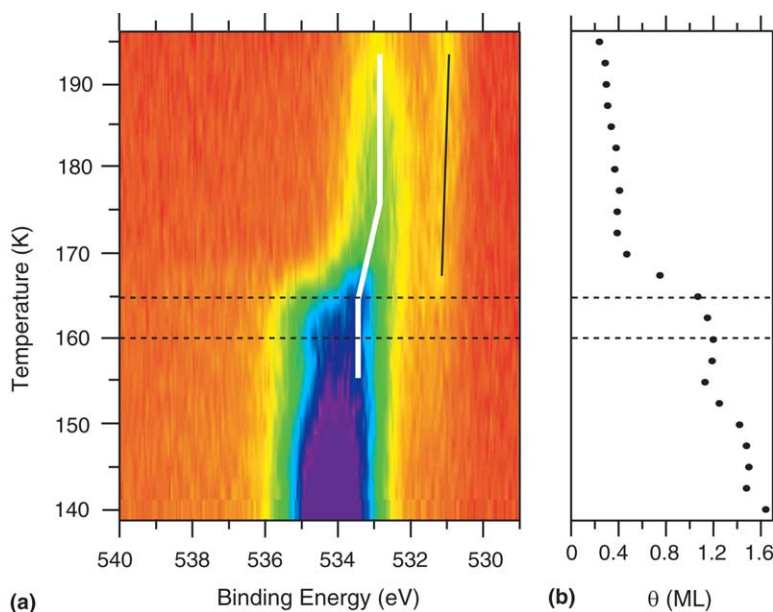


Fig. 2. (a) Temperature programmed XPS study ($\sim 0.07 \text{ K s}^{-1}$, 140–195 K) for D₂O-layer initially adsorbed at 135 K, showing an onset of water dissociation (hydroxyl at $\sim 531.0 \text{ eV}$ indicated with thin solid black line) in the 160–165 K range indicated in the figure by dashed lines. A shift in binding energy of molecular D₂O from 533.4 eV to 532.8 eV, observed with increased temperature and hydroxyl coverage, is indicated with thick solid white line. Each spectrum was taken at a fresh spot on the sample, due to the sample scanning procedure, with a low total 700 eV photon dose generating $0.1 \text{ e}^-/\text{water molecule}$ and recorded at 36 s intervals. (b) Total coverage in ML's during the temperature programmed XPS study. Threshold temperatures for multilayer and monolayer desorption are observed to be around 145 and 165 K, respectively. Partial coverages of OD (hydroxyl) and D₂O for selected temperatures were at 145 K: $\theta(\text{OD}) = 0.02 \text{ ML}/\theta(\text{D}_2\text{O}) = 1.46 \text{ ML}$, 165 K: $\theta(\text{OD}) = 0.07 \text{ ML}/\theta(\text{D}_2\text{O}) = 1.00 \text{ ML}$ and at 195 K: $\theta(\text{OD}) = 0.09 \text{ ML}/\theta(\text{D}_2\text{O}) = 0.15 \text{ ML}$.

age of 0.09 ML at 195 K which is direct evidence for thermally induced partial dissociation of water.¹

The activation barriers toward D₂O-dissociation and desorption were calculated based on the data in Fig. 2. Since the D₂O to OD + D dissociation mechanism has been found to mainly involve an OD-stretch to the substrate [15,16], we use a pre-exponential attempt factor of 10^{13} – 10^{14} s^{-1} . Assuming zero order kinetics, we calculate the

activation barrier towards D₂O dissociation on Cu(110) to be 0.53–0.56 eV. In Fig. 2 we observe the monolayer desorption peak maximum at 168 K. The activation barrier towards desorption was calculated to be 0.50–0.53 eV, irrespective of assuming either zero or first order desorption kinetics, also using a pre-exponential attempt factor of 10^{13} – 10^{14} s^{-1} .

In the temperature dependent XPS study, Fig. 2, we also notice the downward shift in O 1s XPS binding energy (from 533.4 eV to $\sim 532.8 \text{ eV}$) of molecular water in going from the molecularly intact phase to partially dissociated phase. This is similar to what we observe comparing O 1s XPS for the molecularly intact and the heavily beam-damaged (partially dissociated) monolayer in Fig. 1. The downward shift of O 1s XPS binding energy of molecular water in the partially dissociated phase compared to the molecularly intact phase

¹ The same results were obtained for $\sim 1 \text{ ML}$ D₂O samples annealed to 165–170 K without previous exposure to 700 eV photons. That dissociation of D₂O induced by electrons generated from the 700 eV photons was negligible under our sample scanning conditions can also be seen from the XP spectra in Fig. 1(a) which were each, similarly to the XP spectra in Fig. 2(a), recorded at a fresh spot on the sample with the same low total dose of $0.1 \text{ e}^-/\text{water molecule}$.

was also observed comparing the O 1s XP spectra of the two different H₂O-phases on Ru(001) [8]. The observed binding energy shift of molecular water signifies distinct differences in the local bonding environment of molecular water in the molecularly intact compared to partially dissociated phase.

Our results showing intact adsorption of water on clean Cu(110) at low temperatures (<150 K) contradict those in Ref. [3], but can be rationalized based on the sensitivity of water toward X-ray and electron induced dissociation and the likelihood that this indeed influenced their results. At temperatures above 200 K, however, we find a fair agreement with the thermally induced water chemistry on Cu(110) studied in Ref. [3]. The non-dissociative water adsorption on clean Cu(110) below 150 K is consistent with other studies on the same system [17–20,24,25] and partial dissociation at temperatures above 150 K is in good agreement with previous studies reporting water dissociation on clean Cu(110) at temperatures in the 150–180 K range [2,17,18,20]. The activation barrier towards water dissociation is substantially lowered by the presence of atomic oxygen on the surface [2,17–20] and it could be argued that the observed water dissociation on Cu(110) is a result of small amounts of oxygen contamination at the surface [19]. We exclude this possibility in our study based on our estimation of the atomic oxygen contamination as being below 0.1% using high sensitivity XPS.

The dissociation barrier for an estimated low steady state water coverage of approximately 0.001 ML on Cu(110), which would correspond to non-hydrogen-bonded water (i.e. water monomers), has previously been subject to experimental and theoretical studies related to the water–gas shift reaction [26,27]. It has recently been reported both experimentally and theoretically that the dissociation barrier of water can be substantially lowered through the presence of a hydrogen-bonded (HB) water network at the surface [15,28]. Comparing the dissociation barrier for an adsorbed water monomer to the dissociation barrier for water in a saturated two-dimensional (2-D) HB molecularly intact water monolayer, Michaelides et al. [15] found the dissociation barrier of water in the molecularly intact monolayer to be lower by as much as

0.35 eV. Our derived value for the dissociation barrier of 0.53–0.56 eV for D₂O at monolayer coverage on Cu(110) is on the order of 0.3 eV lower than that reported for water monomers of 0.8–0.9 eV [26,27]. Our results are thus consistent with a 2-D HB water network substantially lowering the dissociation barrier of water on Cu(110).

In conclusion we have found using XPS that water adsorbs molecularly on Cu(110) at temperatures below 150 K when sufficient precautions are taken to avoid X-ray and electron induced dissociation and that thermally induced dissociation occurs at temperatures above 150 K. Our findings are consistent with an activated process of water dissociation on clean Cu(110) (atomic O < 0.1%) occurring only above 150 K with a corresponding activation barrier toward dissociation of about 0.53–0.56 eV for D₂O in the saturated 2-D HB-network, similar to what is found for the H₂O/Ru(001)-system. Comparing our results on the water monolayer to previous results for the dissociation barrier of water monomers on Cu(110), i.e. non-hydrogen-bonded water, we find a 0.3 eV lower dissociation barrier for water in the monolayer regime compared to the dissociation barrier previously reported for water monomers. The low activation barrier for water dissociation on Cu(110) and Ru(001) might explain the high sensitivity of the molecularly intact water monolayer on these surfaces toward dissociation induced by X-rays and electrons. The similar magnitudes of the activation barriers towards desorption and dissociation accounts for the fact that water dissociation occurs competitively with desorption for the water monolayer on Cu(110) and the H₂O (not D₂O) monolayer on Ru(001). The high sensitivity of the molecularly intact water monolayer towards X-rays and electrons in combination with the kinetically competitive dissociation/desorption processes may altogether explain the conflicting results in the literature with respect to molecular and dissociative water adsorption.

Acknowledgements

This work was supported by the NSF-CHE-0089215 grant, Swedish Foundation for Strategic

Research, Swedish Natural Science Research Council and the US Department of Energy, Office of Basic Energy Sciences through Stanford Synchrotron Radiation Laboratory and the Advanced Light Source. The staff, David Shuh, Mary Gilles and Tolek Tyliczszak at beamline 11.0.2, Advanced Light Source, as well as the staff at MAX-lab, are gratefully acknowledged.

References

- [1] P.A. Thiel, T.E. Madey, *Surf. Sci. Rep.* 7 (1987) 211.
- [2] A. Spitzer, H. Lüth, *Surf. Sci.* 160 (1985) 353.
- [3] Ch. Ammon, A. Bayer, H.P. Steinrück, G. Held, *Chem. Phys. Lett.* 377 (2003) 163.
- [4] G. Held, D. Menzel, *Surf. Sci.* 316 (1994) 92.
- [5] G. Pirug, C. Ritke, H.P. Bonzel, *Surf. Sci.* 241 (1991) 289.
- [6] P.J. Feibelman, *Science* 295 (2002) 99.
- [7] D.N. Denzler, C. Hess, R. Dudek, S. Wagner, C. Frischkorn, M. Wolf, G. Ertl, *Chem. Phys. Lett.* 376 (2003) 618.
- [8] K. Andersson, A. Nikitin, L.G.M. Pettersson, A. Nilsson, H. Ogasawara, *Phys. Rev. Lett.* 93 (2004) 196101.
- [9] H. Ogasawara, B. Brena, D. Nordlund, M. Nyberg, A. Pelmenschikov, L.G.M. Pettersson, A. Nilsson, *Phys. Rev. Lett.* 89 (2002) 276102.
- [10] P.J. Schmitz, J.A. Polta, S.L. Chang, P.A. Thiel, *Surf. Sci.* 186 (1987) 219.
- [11] K. Kretzschmar, J.K. Sass, A.M. Bradshaw, S. Holloway, *Surf. Sci.* 115 (1982) 183.
- [12] P.A. Thiel, F.M. Hoffmann, W.H. Weinberg, *J. Chem. Phys.* 75 (1981) 5556.
- [13] P.A. Thiel, R.A. DePaola, F.M. Hoffmann, *J. Chem. Phys.* 80 (1984) 5326.
- [14] C. Clay, S. Haq, A. Hodgson, *Chem. Phys. Lett.* 388 (2004) 89.
- [15] A. Michaelides, A. Alavi, D.A. King, *J. Am. Chem. Soc.* 125 (2003) 2746.
- [16] S. Meng, E.G. Wang, C. Frischkorn, M. Wolf, S. Gao, *Chem. Phys. Lett.* 402 (2005) 384.
- [17] C.T. Au, M.W. Roberts, *J. Chim. Phys.* 78 (1981) 921.
- [18] A. Spitzer, H. Lüth, *Surf. Sci.* 120 (1982) 376.
- [19] K. Bange, D.E. Grider, T.E. Madey, J.K. Sass, *Surf. Sci.* 136 (1984) 38.
- [20] M. Polak, *Surf. Sci.* 321 (1994) 249.
- [21] R. Denecke, P. Väterlein, M. Bässler, N. Wassdahl, S. Butorin, A. Nilsson, J.E. Rubensson, J. Nordgren, N. Mårtensson, R. Nyholm, *J. Electron. Spectrosc. Relat. Phenom.* 101–103 (1999) 971.
- [22] M.J. Bozack, L. Muehlhoff, J.N. Russel Jr., W.J. Choyke, J.T. Yates Jr., *J. Vac. Sci. Technol. A* 5 (1987) 1.
- [23] C. Harendt, J. Goschnick, W. Hirschwald, *Surf. Sci.* 152/153 (1985) 453.
- [24] D. Lackey, J. Schott, B. Straehler, J.K. Sass, *J. Chem. Phys.* 91 (1989) 1365.
- [25] F. Benseba, T.H. Ellis, *Prog. Surf. Sci.* 50 (1995) 173.
- [26] J. Nakamura, J.M. Campbell, C.T. Campbell, *J. Chem. Soc. Faraday Trans.* 86 (1990) 2725.
- [27] G. Wang, L. Jiang, Z. Cai, Y. Pan, X. Zhao, W. Huang, K. Xie, Y. Li, Y. Sun, B. Zhong, *J. Phys. Chem. B* 107 (2003) 557.
- [28] H.S. Kato, S. Shiraki, M. Nantoh, M. Kawai, *Surf. Sci. Lett.* 544 (2003) L722.